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THE EMISSION SPECTROCHEMICAL ANALYSIS OF IMPURITIES IN PLUTONIUM DIOXIDE

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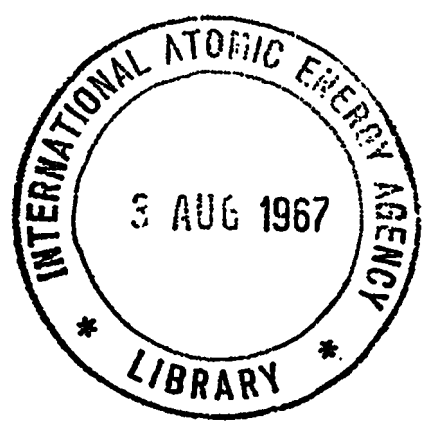

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ABSTRACT

A description is given of a method used at the A.A.E.C. Research Establishment for the analysis of impurities in plutonium dioxide.

Plutonium is separated from its impurities by adsorption on to anion - exchange resin. The effluent containing the impurities is spectrographically analyzed using a graphite spark technique. Pyrolytic graphite electrodes which are non-porous and do not require sealing are used in preference to the normal greased electrodes which are unsuitable for the analysis of acidic solutions.

The plutonium is analyzed for Fe, Al, Mg, Mn, Ni, Cr, Pb, Cd, Co, Ca, Sn, Mo, and Zn using vanadium as internal standard. The overall precision of the method is estimated to be ± 20 per cent.

CONTENTS

1. INTRODUCTION

The spectrographic analysis of plutonium is complicated by the radiological health hazard associated with its handling and, in the case of excitation, its complex spectrum. The usual carrier distillation procedure for analyzing refractory materials is not readily adaptable to plutonium dioxide because of the lack of impurity standards and because of the significant health hazard associated with the possible volatilization of milligram quantities of the material.

The method used by most workers for the determination of impurities in plutonium compounds is an ion-exchange separation of the impurities followed by spectrographic analysis (Wenzel and Pietri 1964, Buchanan et al. 1958, Ko 1958). Plutonium in the IV oxidation state is strongly adsorbed onto anion-exchange resin in the nitrate form while all impurities with the exception of silicon and boron pass quantitatively through the column. For the determination of silicon and boron a cation-exchange separation is used.

Wenzel and Pietri have adequately described the procedure for analysing plutonium compounds. They used the sensitive direct current arc in the spectrographic analysis of 23 elements. Since americium-241 is not adsorbed onto the column and is therefore present in the effluent together with a small quantity of plutonium not adsorbed, extensive containment of the arc chamber is required for the safe excitation of the samples. At the New Brunswick Laboratory, excitation is carried out in a separate room and, by a series of windows, lenses, and mirrors, the spectra are recorded in another room. It is difficult to achieve suitable spectral line uniformity which is necessary for densitometric work.

At the A.A.E.C. Research Establishment, facilities for active spectrographic analysis do not permit such extensive modifications to instrumentation or laboratory area. Adequate facilities are available for sample preparation including dissolution, ion-exchange separation, and evaporation. On the other hand, for spectrographic analysis of the samples it was necessary to construct a separate glove box with excitation facilities so that the general purpose arc chamber would not become contaminated.

To minimize the health hazard associated with excitation of the samples the sensitive graphite spark technique was used. This was regarded as safer and less complicated so far as construction of the glove box was concerned. The glove box was designed on the same optical principle as the general purpose arc chamber, obviating any difficulties with optical alignment and ensuring correct spectral line uniformity. Ready interchangeability of the two boxes has also ensured rapid processing of future samples.

2. ANION-EXCHANGE SEPARATION

2.1 Reagents

Anion-exchange resin A.R. AG7-X10 (chloride form) 200-400 mesh. (Bio-Rad Laboratories, California, U. S. A.).

Distilled A.R. nitric acid - 15N

Distilled A.R. hydrochloric acid - 10N

A.R. hydrofluoric acid - 40 per cent.

Hydrogen peroxide - 30 per cent.

Internal standard solution - 20 p.p.m. V in 1N HNO_3

2.2 Anion-Exchange Resin Preparation

The anion-exchange resin was washed several times in distilled water followed by several washings in 8N nitric acid until no positive chloride reaction with silver nitrate solution was obtained. It was then washed and stored in distilled water in a polythene container.

Correct treatment of the resin is necessary for complete retention of plutonium on the column. The stored resin was well washed with 8N nitric acid before the column was charged. It was found that to achieve satisfactory flow rates (0.1 ml/min) it was necessary to increase the dimensions of the column (see Figure 1). The slow rates experienced with the recommended column were attributed to the very fine mesh size of the resin. It is therefore recommended that a resin of 50-100 mesh be used in future.

When the column is charged it should be used immediately as the nitric acid causes decomposition, evidenced by the darkening of the resin and the presence of an oily substance in the effluent.

2.3 Dissolution

Methods for dissolving high fired plutonium dioxide, including aqueous and fusion techniques, have been investigated by Black and Drummond (1965). However in our laboratory facilities were available only for simple aqueous dissolutions. The plutonium dioxide (2.5g) was dissolved in 15N nitric acid containing 0.05M hydrofluoric acid by boiling under reflux. The fluoride ion acts as a catalyst and, owing to its reaction with the glassware, its concentration was maintained by dropwise addition at intervals. This fluoride ion concentration must not be exceeded or the solubility product of the fluoro-complex will be exceeded with resultant precipitation.

Most of the PuO_2 dissolved after six hours' treatment and the remainder

required a further twelve hours. The solution was evaporated to a small volume (≈ 10 ml) by distillation of the nitric acid. It was then made up to 100 ml with 8N nitric acid. The solution should not be taken to dryness because partial decomposition to the oxide may occur and require a repetition of the nitric-hydrofluoric acid dissolution step.

2.4 Elution of Plutonium Solution

An aliquot (20 ml) equivalent to 500 mg PuO_2 was taken and 30 per cent. H_2O_2 (5 ml) was added to convert the Pu to the IV oxidation state. The excess peroxide was removed by gently heating under an infra-red lamp. The green solution was cooled and added to the ion-exchange column.

The first 5 ml of effluent was discarded and the remainder collected in a covered beaker. Quantitative elution of the impurity cations was carried out with two 25 ml additions of 8N HNO_3 to the column. The green band of Pu on the resin was retained in the upper half of the column.

When all the effluent had been collected the plutonium was removed from the column by several washings with 0.35N HCl/0.05N HF solution.

2.5 Preparation of Electrodes

The effluent was filtered through a sintered glass filter funnel to remove small particles of resin. The filtrate was evaporated to dryness but not baked; it was cooled and 1 ml of the 20 p.p.m. vanadium internal standard solution added. The solution was swirled around the dish to dissolve all the residue and 0.1 ml aliquots were pipetted onto the electrodes and dried.

A blank sample of 70 ml 8N HNO_3 was similarly treated under identical working conditions.

3. SPECTROGRAPHIC ANALYSIS

3.1 Preparation of Standards

A master standard solution was prepared at the following concentrations:

1000 p.p.m : Fe	(A)
200 p.p.m. : Al, Ca, Cr, Mg, Mn, Na, Ni, Pb, Sn, Zn	(B)
20 p.p.m. : Cd, Co, Cu, Mo.	(C)

Spectroscopically pure chemicals were used and dissolved in the minimum amount of concentrated nitric acid before dilution with 1N nitric acid. A range of standards was prepared by dilution with the 20 p.p.m. internal standard vanadium solution in 1N nitric acid.

The ranges covered were:

A	50, 100, 250, 500 p.p.m.
B	10, 20, 50, 100 p.p.m.
C	1, 2, 5, 10 p.p.m.

3.2 Use of Pyrolytic Graphite Tops

Sealed graphite, copper, and silver flat top electrodes are unsuitable for the analysis of nitric acid solutions. In the case of sealed graphite electrodes, breakdown of the sealant occurs with resultant absorption of sample into the electrode. Copper and silver are unsuitable owing to reaction with the electrode material forming porous deposits which result in high total solids.

Since pyrolytic graphite is non-porous and inert to acid attack, it was considered to be the most suitable material for this type of analysis. Pyrolytic graphite tops (1 cm dia. and about 0.5 mm thick) were cut from slabs * and glued onto 1/4 inch dia. graphite rods with C-9 cement. †

3.3 Choice of Excitation Conditions

Both high voltage spark and pulsed arc excitation were investigated for sensitivity and reproducibility. Pulse parameters were varied to determine optimum conditions, and spectral line intensities of several elements were considered for both single and double pyrolytic graphite electrodes. In the former case the effect of the geometry of the counter electrode was also considered. The single pyrolytic electrode was found to be more reproducible and the effect of changing the geometry of the counter electrode did not increase the sampling area of the analysis electrode.

The suitability of the internal standard was examined for both high voltage spark and pulsed arc conditions by calculating the coefficient of variation of the ratio of the relative intensities of the spectral lines of the element and the internal standard. The choice of spectral line was also examined. The results ranged from 5 to 30 per cent. for both methods but the spark excitation was selected because of its generally better reproducibility and sensitivity over the range of elements.

3.4 Recovery

The quantitative elution of impurity cations from the resin was checked by passing a known standard through the column. Recoveries of between 95 and 105 per cent. indicated that quantitative recoveries were achieved.

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* Supplied by the Super-Temp Corporation, California, U.S.A.

† Supplied by National Carbon Company.

3.5 Spectrographic Conditions

Table 1 gives the spectrographic conditions.

TABLE 1

SPECTROGRAPHIC CONDITIONS

Spectrograph	3.4M Ebert, plane grating, 600 lines/mm (Jarrell-Ash Co.).
Grating Angle	5.77° (2200-4600Å, first order).
Source	High Voltage Spark, L = 250μH C = 0.005μF.
Slit	2 x 0.04 mm.
Gap	2 mm.
Exposure	30 sec.
Electrodes	Sample: 3/8 inch dia. pyrolytic graphite top cemented onto 1/4 inch dia. National SPK rod. Counter: 120° cone (National AGKSP 1/4 inch dia.).
Emulsion	Ilford Zenith Astronomical
Calibration	7 stepped sector, Fe electrodes, under above conditions, 15 sec. exposure. Triplicate exposures of each standard and samples are made.

The lower limits of detection of impurities, using these conditions are given in Appendix 3.

3.6 Working Curves

Working curves were constructed by plotting the ratio (relative intensity analytical line) / (relative intensity internal standard line) against concentration of the element. Figures 2, 3 and 4 are typical working curves for Fe, Ni, and Cu respectively.

To test the optical interchangeability of the two boxes, ratios were taken for the standards exposed in the general purpose box and, after a four month interval, in the Pu box.

The results are summarized in Table 2 which indicates the stability of the calibration and the complete interchangeability of the boxes.

TABLE 2

INTERCHANGEABILITY OF EXCITATION GLOVE BOXES

	RATIO $\frac{\text{RI Mn2801}}{\text{RI V2894}}$ *		RATIO $\frac{\text{RI Fe 2599}}{\text{RI V2688}}$	
Standard	General Purpose Box	Pu Box	General Purpose Box	Pu Box
B	2.48	2.63	7.39	7.12
C	1.27	1.40	4.80	5.66
D	0.55	0.60	2.25	2.27
E	0.38	0.35	1.25	1.22

* mean of triplicate exposures.

3.7 Results

The two samples of plutonium dioxide were analysed for all impurities covered by the standards except sodium. Analysis for silicon and boron could not be carried out because hydrofluoric acid was used in the dissolution step.

The results for 2 samples are given in Table 3, expressed as parts per million on a plutonium metal basis. The results have been corrected for blanks and are estimated to have a precision of ± 20 per cent. They may be compared with a typical PuO_2 batch analysis in Appendix 1.

TABLE 3

RESULTS OF ANALYSIS OF PuO_2 SAMPLES

(Expressed as p.p.m. on metal basis)

Element	Batch FF 149	Batch FF 150
Fe	190	180
Mg	40	90
Mn	5	10
Al	130	140
Ni	10	10
Ca	10	10
Cu	35	30
Zn	60	60
Cr	5	5
Sn	10	10
Pb	10	10
Co	10	10
Cd	N(< 5)	N(< 5)
Mo	N(< 2)	N(< 2)

N = not detected

4. DISCUSSION OF RESULTS

The accuracy of the analysis may have been affected by the presence of a yellow deposit on the electrodes. The relative intensities of the analytical and internal standard lines were lower in the exposures of the samples than those of the standards. This is typical of the graphite spark technique when the total solids are high. The decrease in intensities is due to loss of the sample from the electrode top by physical disruption of the sample by the spark discharges.

The yellow deposit was first thought to be organic matter formed by breakdown of the resin in the nitric acid but this was discounted when a standard containing organic matter showed no such reduction in intensity. Consideration was then given to the amount of americium present in the effluent. Total α - counts of each effluent sample revealed that up to 30 µg Am-241 was present on

each electrode. The observed intensity of the internal standard lines was slightly higher in the samples with the lower americium content, suggesting that its presence contributed to the decrease in intensity of the sample exposures. This, together with sodium contamination from the glassware, was considered to be responsible for the build-up of solids on the electrodes.

The separation of Am-241 (Katz and Seaborg 1957) from the effluent requires conversion to the VI state with oxidizing agents followed by ion-exchange or solvent extraction. No reagent is suitable in this case, in view of the need to avoid contamination and to keep the total solids low. The observed decrease in intensity of the analytical lines of the sample exposures was compensated by a decrease in the intensities of the internal standard lines. The ability of the internal standard to compensate for variable intensities was established from exposures of the standards.

The blank corrections were composed of reagent blanks and contamination from the preparation glove boxes. In some cases, particularly for calcium and magnesium, the blank and impurity levels were of the same order, so that the error in these cases may be higher than the estimated ± 20 per cent. No HF was used in determining the blank since the amount added during the dissolution step was used up by reaction with glassware and also in the formation of the fluoro-complex. Although reaction with the glassware could yield blanks for impurities such as calcium and magnesium it was considered that these would be small in comparison with the blanks due to reagents and glove box operations.

5. CONCLUSION

The anion-exchange resin separation of plutonium and its impurities, coupled with the sensitive graphite spark technique, has been applied at the A.A.E.C. Research Establishment, to the analysis of plutonium dioxide. The plutonium was analyzed for Fe, Al, Mg, Mn, Ni, Cr, Pb, Cd, Co, Ca, Sn, Cu, Mo and Zn using V as an internal standard. The nitric-hydrofluoric acid dissolution of the samples excluded the analysis of silicon, sodium, and boron due to reaction with the glassware. The method is however applicable to the analysis of silicon and boron in plutonium metal.

In these laboratories requirements for plutonium analysis are not frequent and the method is most suitable for rapid processing of samples owing to the ready interchangeability of the excitation glove box. This obviates the need for a separate spectrographic plutonium facility.

6. ACKNOWLEDGEMENT

We wish to express our thanks to the Process Chemistry Group for provision of the sample preparation facilities and helpful suggestions in glove box techniques and to J. Kennedy for construction of the spark box.

7. REFERENCES

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APPENDIX 1

REPRESENTATIVE COMPOSITION FOR PLUTONIUM DIOXIDE †

(Values expressed in parts per million on the oxide basis*)

Fe	80-250
Mn	10-30
Cr	30-50
Al	5-30
Si	10
Mg	<50
B	< 1
Cd	< 1

All other unspecified cations <20 each

* oxide to metal conversion factor = 1.13

† typical batch analysis of NUMEC plutonium dioxide

APPENDIX 2

TABLE OF ANALYTICAL LINES

ELEMENT	LINE (Å)	V INTERNAL STANDARD LINE (Å)
Fe	3020.640	3102.299
	2598.369	2687.956
Al	3082.155	3102.299
Cu	3273.962	3276.124
Mg	2852.129	2893.320
Mn	2801.064	2893.320
Ca	3179.332	3185.396
Na	3302.323	3276.124
Zn	2801.056	2893.320
	3345.572	3276.124
Cr	2835.633	2893.320
Ni	3050.819	3102.299
Pb	2833.069	2893.320
Sn	2839.989	2893.320
Cd	3261.057	3276.124
Co	3405.120	3276.124
Mo	3170.347	3185.396

APPENDIX 3

ESTIMATED DETECTION LIMITS* FOR VARIOUS ELEMENTS USING THE GRAPHITE SPARK METHOD

Element	µg on Electrode
Al	0.02
Ca	0.002
Cd	0.03
Co	0.005
Cr	0.003
Cu	0.002
Fe	0.3
Mg	0.001
Mn	0.05
Mo	0.01
Ni	0.03
Pb	0.2
Sn	0.08
Zn	0.1

* Based on exposures of standard solutions.

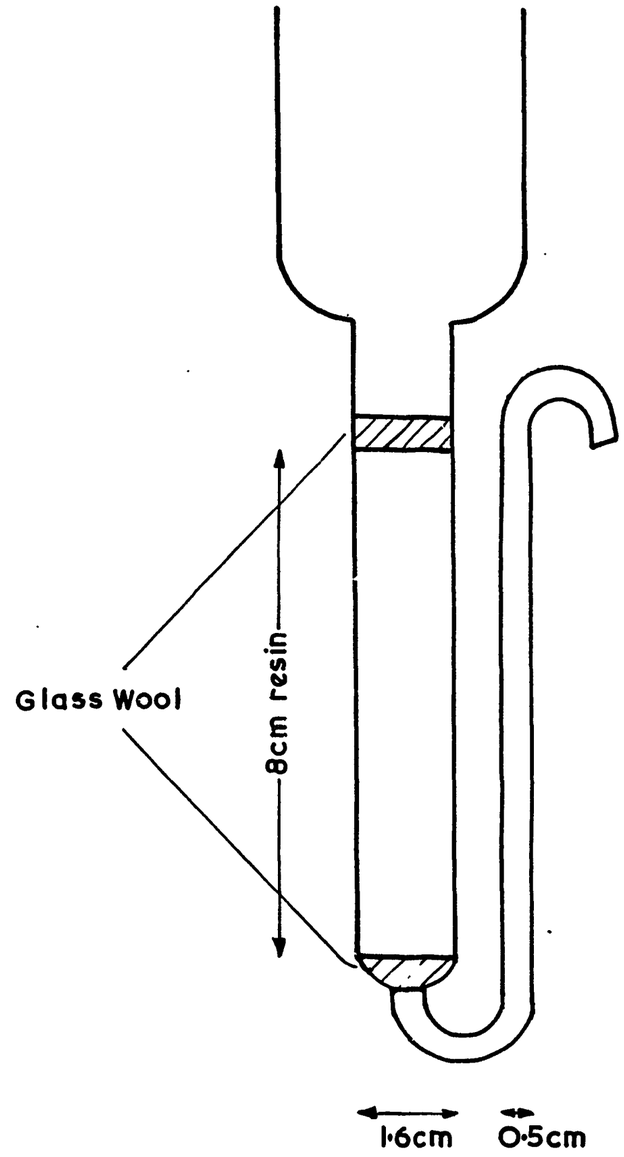

FIGURE 1. SELF-LEVELLING ION EXCHANGE COLUMN

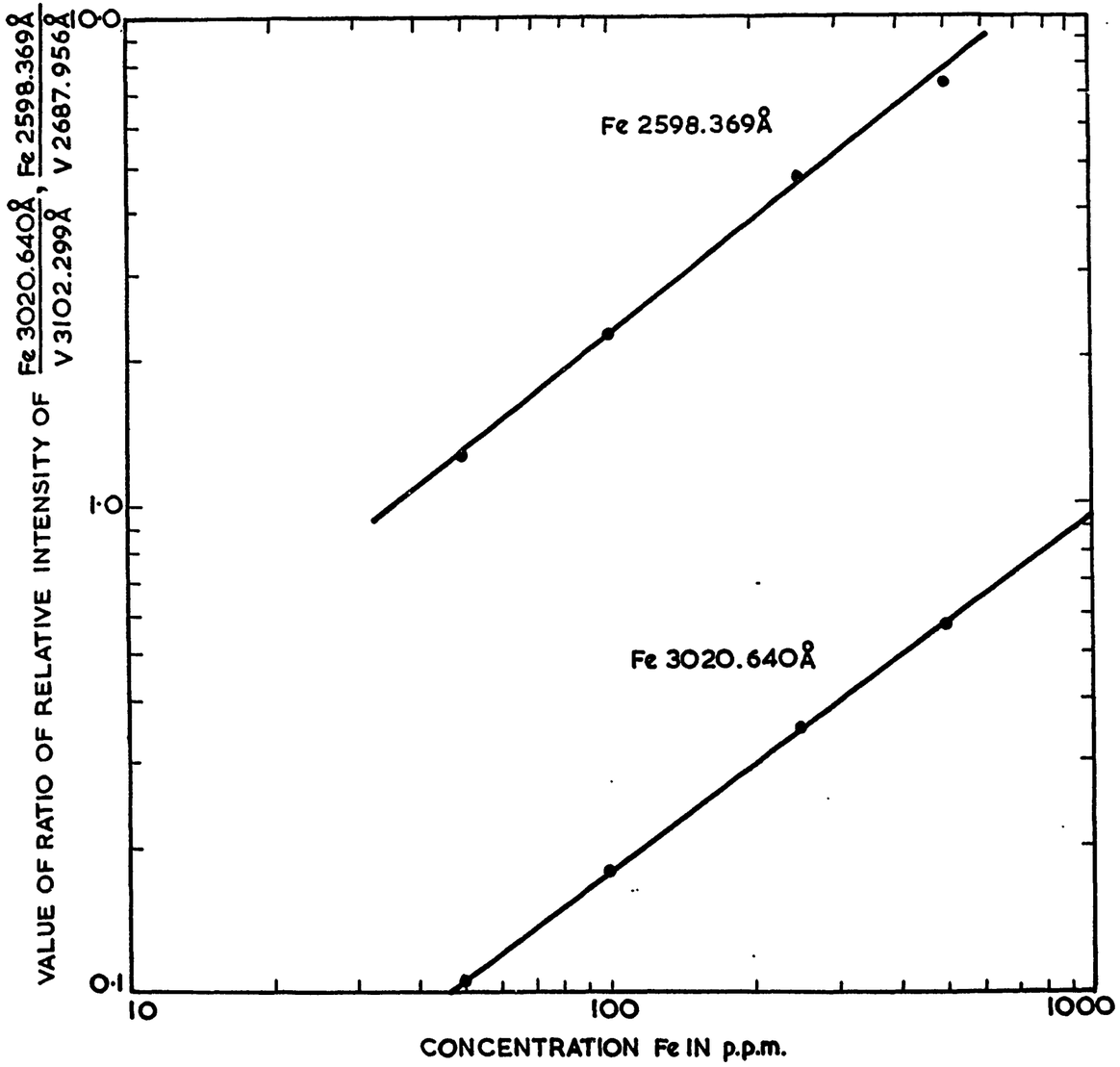

FIGURE 2. CALIBRATION CURVES FOR ANALYSIS OF IRON BY THE GRAPHITE SPARK METHOD

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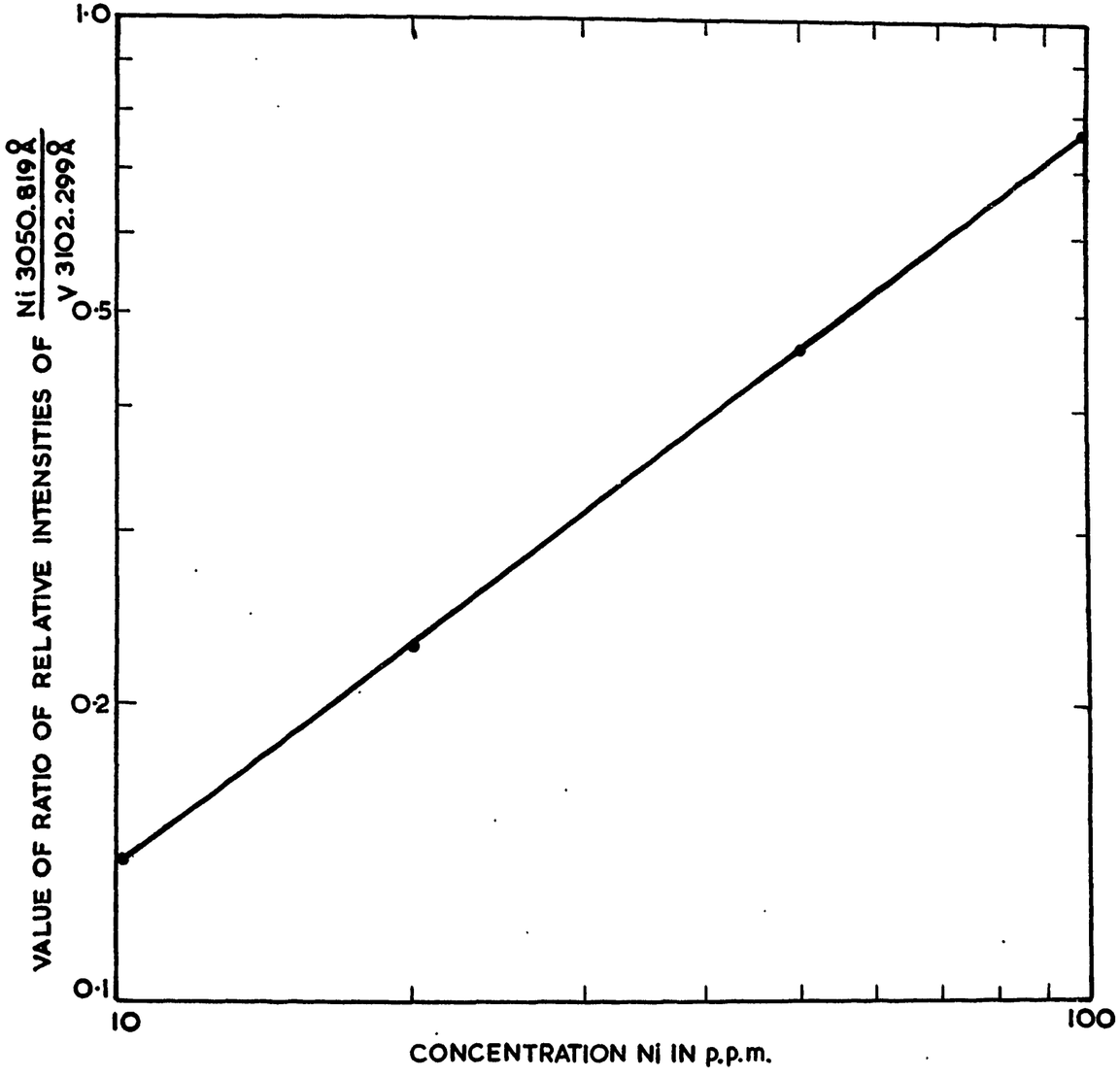

FIGURE 3. CALIBRATION CURVE FOR ANALYSIS OF NICKEL BY THE GRAPHITE SPARK METHOD

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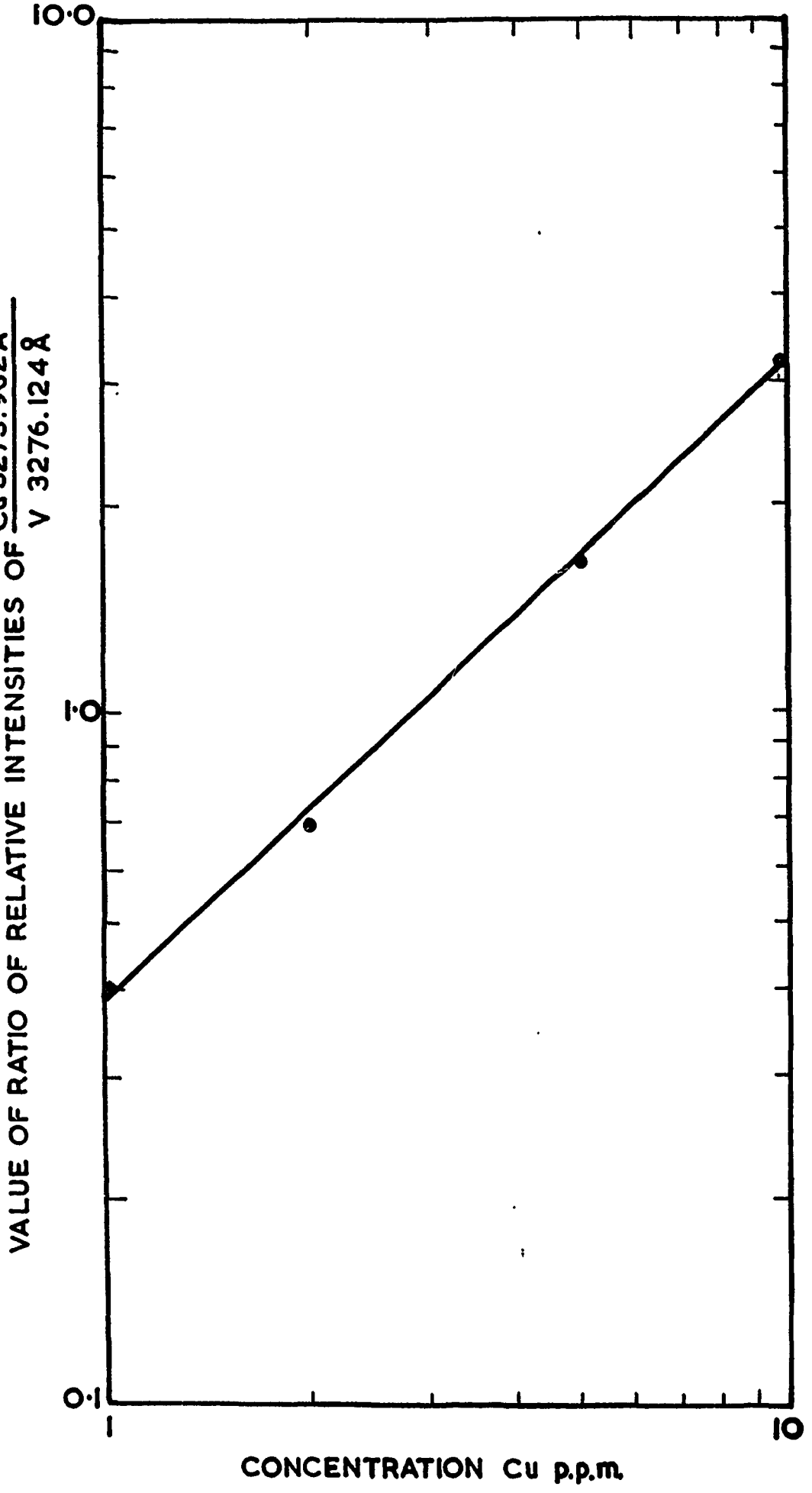

FIGURE 4. CALIBRATION CURVE FOR ANALYSIS OF COPPER BY THE GRAPHITE SPARK METHOD

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